(19) Canadian Intellectual Property Office
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(11) CA 2 087 972 (13) C

(40) 04.01.2000
(43) 24.01.1992
(45) 04.01.2000

(12)

(21) 2 087 972

(22) 23.07.1991

(51) Int. Cl.[6]: B01D 053/047

(85) 22.01.1993

(86) PCT/CA91/00258

(87) WO92/01504

(30) 07/557,132 US 23.07.1990

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(54) EXTRACTION ET CONCENTRATION D'UN ELEMENT GAZEUX
(54) EXTRACTION AND CONCENTRATION OF A GAS COMPONENT

(57) Pressure swing adsorption separation of a gas mixture, containing a first component and also a second component which may be at low or trace concentrations, is performed to extract the second component from the gas mixture so that a first product stream containing the first component may be substantially purified with respect to the second component, while the second component is concentrated to a high degree in a second product stream. Gas mixtures containing three components may also be separated. The apparatus of the invention performs the separation within a single working space.

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(12) (19) (CA) **Brevet-Patent**

(11) (21) (C) **2,087,972**
(86) 1991/07/23
(87) 1992/01/24
(45) 2000/01/04

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(51) Int.Cl.[6] B01D 53/047
(30) 1990/07/23 (07/557,132) US

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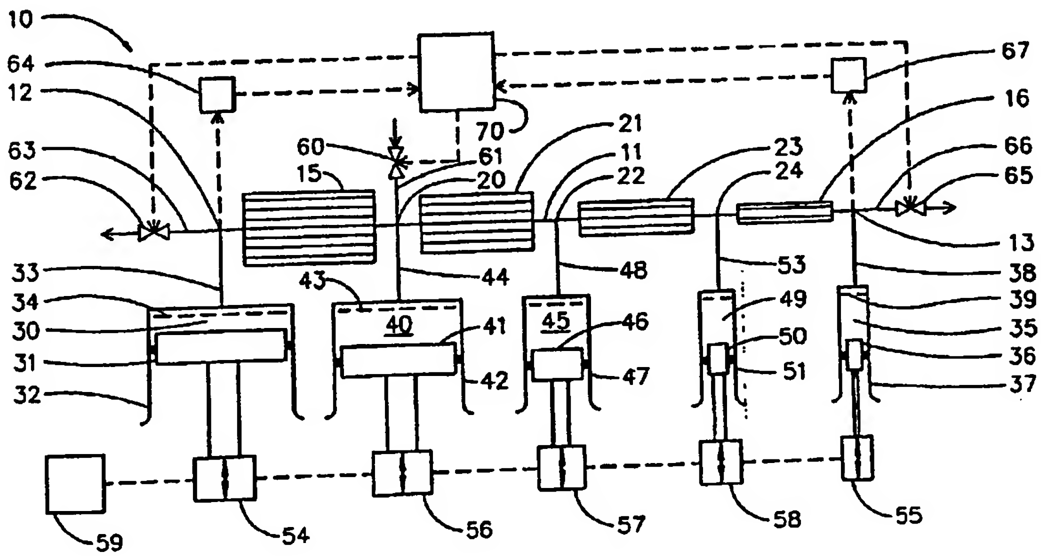

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PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B01D 53/04 2087972	A1	(11) International Publication Number: WO 92/01504 (43) International Publication Date: 6 February 1992 (06.02.92)

(21) International Application Number: PCT/CA91/00258

(22) International Filing Date: 23 July 1991 (23.07.91)

(30) Priority data:
557,132 23 July 1990 (23.07.90) US

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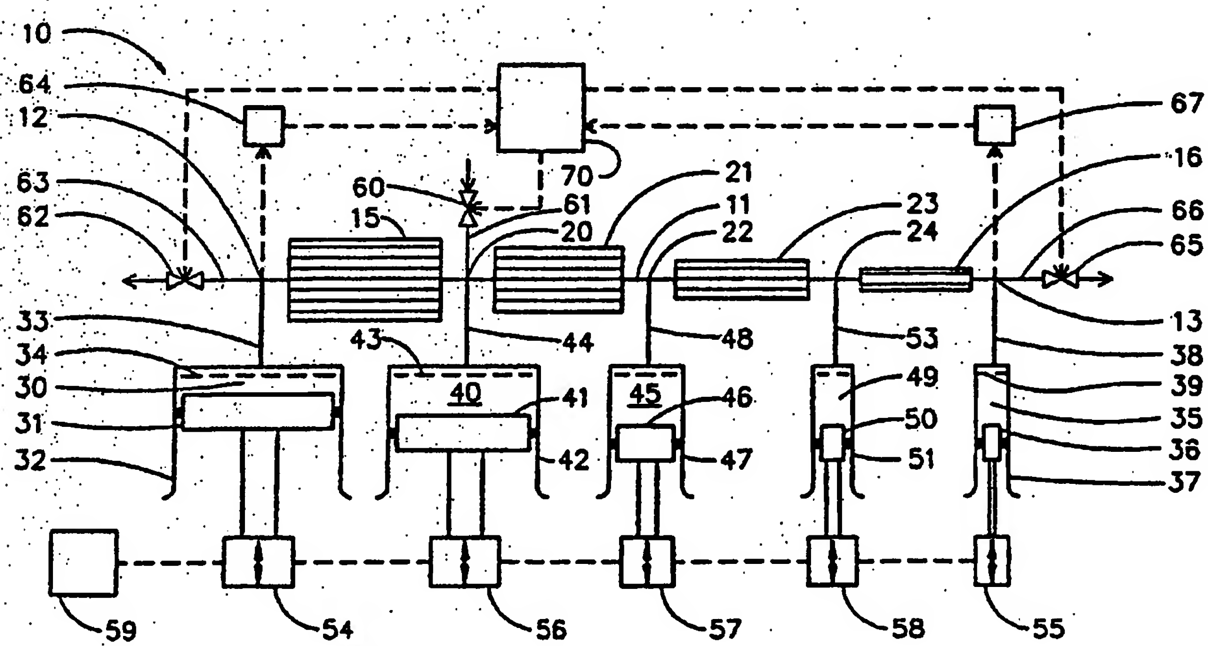
(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

Published
With international search report.

(54) Title: EXTRACTION AND CONCENTRATION OF A GAS COMPONENT



(57) Abstract

Pressure swing adsorption separation of a gas mixture, containing a first component and also a second component which may be at low or trace concentrations, is performed to extract the second component from the gas mixture so that a first product stream containing the first component may be substantially purified with respect to the second component, while the second component is concentrated to a high degree in a second product stream. Gas mixtures containing three components may also be separated. The apparatus of the invention performs the separation within a single working space.

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EXTRACTION AND CONCENTRATION OF A GAS COMPONENT

TECHNICAL FIELD

The invention relates to separations conducted in the gas or vapour phase, and particularly to extraction and concentration of a component initially present at low or trace concentrations. The component to be extracted and concentrated may be a valuable substance whose recovery and concentration to useful levels is desired, or may be a toxic or environmentally deleterious substance whose removal and concentration for disposal is required.

BACKGROUND ART

Gas separation by pressure swing adsorption is achieved by coordinated pressure cycling and flow reversals over an adsorbent bed which preferentially adsorbs a more readily adsorbed component relative to a less readily adsorbed component of the mixture. The total pressure is elevated during intervals of flow in a first direction through the adsorbent bed, and is reduced during intervals of flow in the reverse direction. As the cycle is repeated, the less readily adsorbed component is concentrated in the first direction, while the more readily adsorbed component is concentrated in the reverse direction.

The conventional process for gas separation by pressure swing adsorption uses two or more adsorbent beds in parallel, with directional valving at each end of each adsorbent bed to connect the beds in alternating sequence to pressure sources and sinks, thus establishing the changes of working pressure and flow direction. Typically, the desired product is the less readily adsorbed fraction, which has been purified by substantial removal of the more readily adsorbed component. If the

desired product component is present as a large fraction (greater than about 10% or 20%) of the feed gas mixture, and the adsorbent is sufficiently selective between the components, the desired product component can be purified to a high degree, although only incompletely recovered since some of the product is used to purge the adsorbent bed and is exhausted. If the component to be separated is present only as a small fraction (less than 1%) of the feed gas mixture, the conventional process cannot achieve satisfactory concentration of this component.

The prior art includes pressure swing adsorption devices with improved capability for approaching complete separation of binary mixtures. Keller (U.S. Pat. No. 4,354,859) has disclosed a single bed pressure swing adsorption device, with mechanical volume displacement means cycling at the same frequency at both ends of the adsorbent bed, and with a specified range of phase angles between the two volume displacement means which are required to have unequal displacements, such that the displacement ratio of the smaller to the larger volume displacement means is in the specified range of about 0.15 to 0.65. The volume displacement means may be pistons or diaphragms. The feed mixture is introduced to an intermediate point of the adsorbent bed, and the product components are separated to either end. Keller showed experimentally that his device could achieve approximately complete separation of gas mixtures such as dry air and a 50/50 mixture of hydrogen and methane. My international application PCT/GB88/00897 discloses other related devices, including a gas separation apparatus with two interconnected adsorbent beds cooperating with three cyclic volume displacement means to separate the components of a binary gas mixture with simultaneous high recovery and purity.

Other devices using cyclically operated volume displacement means at both ends of an adsorbent bed are disclosed in my U.S. Pat. No. 4,702,903 in which a temperature gradient is imposed on the adsorbent bed, my U.S. Pat. No. 4,801,308 in which the adsorbent bed is itself cyclically expanded and contracted, and my U.S. Pat. No. 4,816,121 which is concerned with separation of chemically reactive gases.

Relative to the above cited prior art, the present invention provides an improved process and apparatus for separating the components of binary or ternary gas mixtures with simultaneous substantial purification and high recovery of the components, particularly in applications where one component is initially present at low or trace concentrations. While prior art adsorptive gas separation systems using a single working volume are capable of purifying a carrier gas and removing a trace gas phase component to a high degree, they have not been capable of simultaneously concentrating the trace component to a high degree, as is achieved in the present invention.

DISCLOSURE OF INVENTION

In a single working volume, this device has a flow path through a series of interconnected adsorbent beds or adsorbent bed segments. The apparatus of this invention has at least three interconnected adsorbent bed segments in the working volume. The flow path has two ends, or may be branched to have three or more ends. A number of reciprocating cyclic volume displacement means are provided to generate cyclic pressure variations and coordinated flow reversals in the flow path. The cyclic volume displacement means each change the volume of a working space, which is part of the working volume and is

connected to an end of the flow path or to a node in the flow path at the interconnection between adjacent adsorbent beds.

The volume displacement means associated with the working volume all reciprocate at the same frequency, but with a phase difference between at least two cyclic volume displacement means at opposite ends of the flow path. The working space of the volume displacement means at an end of the flow path which reciprocates with its volume changes in relatively leading phase will be referred to as the expansion space, and the working space of the volume displacement means at the opposite end of the flow path which reciprocates with its volume changes in relatively lagging phase will be referred to as the compression space. The volume variations of volume displacement means at intermediate nodes in the flow path may be in phase with either the compression or expansion space, or may have a phase intermediate between the compression and expansion spaces.
The feed gas mixture is introduced by feed supply means to an intermediate node in the flow path, and product streams concentrated in either of the respectively more readily and less readily adsorbed fractions are withdrawn by product delivery means connected to the opposite ends of the flow path. The more readily adsorbed or heavy component is concentrated in the heavy product withdrawn adjacent the compression space, and the less readily adsorbed or light component is concentrated in the light product withdrawn adjacent the expansion space.

Product delivery valves and valve control means are incorporated in the product delivery means, to control the mass flow rates of the heavy and light products so that desired high purity and recovery of the heavy and light components in respectively the heavy and light products is achieved. For combined high concentration

and recovery of both components in the respective products, the mass flow ratio between light and heavy products should be approximately equal to the feed composition ratio of light and heavy components. For highest concentration and purity of either light or heavy component in the corresponding light or heavy product, the flow of that product relative to the other product will be reduced somewhat below the theoretical ratio indicated by the feed concentration ratio, thus enhancing the purity of one product at the cost of reducing both the recovery of that component and the purity of the other product.

The adsorbent beds and working spaces of volume displacement means along the flow path may be sized in approximate correspondence to the gas mixture composition and product flow ratio. In applications where the feed composition ratio is greatly asymmetric, so that one of the heavy or light components is a minority component, and the other a majority component, the adsorbent bed and variable volume working space at the end of the flow path to which the minority component is concentrated will be much smaller than the adsorbent bed and working space at the end of the flow path to which the majority component is concentrated. Only one adsorbent bed will typically be used to concentrate and purify the majority component between the feed supply node and the product delivery end for the majority component. However multiple adsorbent beds, with intermediate variable volume working spaces at their interconnection nodes, may be used to achieve a large concentration ratio for a small minority component, with the adsorbent beds and intermediate working spaces being stepped down to smaller sizes in sequence from the feed supply node to the product delivery end for the minority component. As the minority component becomes more concentrated along the flow path, the adsorbent bed cross-section is stepped down with smaller variable

volume working spaces also stepping down to the minority component product delivery end.

Thus, the adsorbent bed is tapered to be widest at the feed and majority product delivery ends, and smallest at the minority product delivery end. If the minority component is a smaller fraction of the feed, the ratios of adsorbent size and working space displacement from the minority product delivery end to the majority product delivery end become smaller, and more intermediate nodes become necessary or desirable to step down from the feed supply node to the minority product delivery end.

When the ratio of minority to majority components in a binary mixture is in the range of 1:10 to 1:100, the apparatus may incorporate two stepped adsorbent beds to concentrate the minority component, one adsorbent bed to purify the majority component, and four variable volume spaces at the ends and intermediate nodes of the flow path. When the ratio of minority to majority components becomes more extreme, i.e. of the order 1:1000, three or more stepped adsorbent beds may be needed to achieve a high final concentration of the minority component in the minority product.

An apparatus according to the invention for separating and concentrating the three components or fractions of a ternary gas mixture has a branched flow path, so that three flow path ends, each having an adsorbent bed and a variable volume space with a volume displacement means, are provided. A first component which is either more or less readily adsorbed than the second and third components is introduced to the flow path at a point between the first end of the flow path to which the first product is concentrated, and the intermediate node from which the second and third flow paths branch and past which only the second and third components are allowed to

pass for subsequent separation between the second and third flow path ends.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a simplified schematic of an apparatus with four adsorbent beds in a single flow path, for extracting and concentrating a trace component from a feed gas mixture.

Fig. 2 shows an apparatus with four adsorbent beds, using a stepped piston for mechanical simplicity.

Fig. 3 shows an opposed pair of gas separators with hydraulic displacement means to establish pressure cycling and a suitable displacement phase relationship.

Fig. 4 shows a cascaded pair of gas separators for achieving high purity separation of both components of a gas mixture.

Fig. 5 shows an apparatus for separating the three components of a ternary gas mixture.

MODES FOR CARRYING OUT THE INVENTION

Fig. 1

A pressure swing adsorption apparatus 10 has a flow path 11 within the working space of the apparatus, the flow path having a first end 12 and a second end 13. The flow path passes through a number "N" of adsorbent beds or adsorbent bed segments in series, with intermediate nodes of the flow path between each adjacent pair of adsorbent beds. In the present invention, there are at least three adsorbent beds in the flow path; and in the particular embodiment of Fig. 1, N = 4. The junctions in the flow path between adjacent adsorbent beds will be referred to as intermediate nodes of the flow path. The intermediate nodes are junctions where cyclically varied volumes communicate with the flow path, or where feed gas is introduced to the flow path, or where the flow path may be branched; and where the adsorbent bed cross-section may be stepped.

The adsorbent bed adjacent the first end 12 of the flow path will be referred to as the first adsorbent bed 15, while the adsorbent bed adjacent the second end 13 of the flow path is the second adsorbent bed 16. The first adsorbent bed 15 carries the flow path from its first end 12 to a first intermediate node 20, communicating with a first intermediate adsorbent bed 21 which carries the flow path to a second intermediate node 22, in turn communicating with a second intermediate adsorbent bed 23 which carries the flow path to a third intermediate node 24.

It will be understood that the flow path, in passing through an adsorbent bed, becomes in general a large number or network of similar narrow channels in parallel, so that the gas mixture in the flow path is

brought into intimate contact with the adsorbent material supported in the adsorbent bed, and with the entire flow path passing thus through the adsorbent bed so that there is substantially no bypassing of the flow path past an adsorbent bed. The adsorbent bed may be constituted as a packed bed of adsorbent pellets, or as a parallel channel monolithic structure. In either case, substantial geometrical similarity of the adsorbent bed channels is required to minimize axial dispersion and mixing in the flow path.

The adsorbent beds of the present invention may be separate adsorbent beds in distinct housings connected by conduits serving as the intermediate nodes, or may be segments of a single extended adsorbent column in a single housing. Each adsorbent bed (or adsorbent bed segment) is defined here to terminate at an intermediate node, regardless of whether the beds are physically separated or are segments of an extended adsorbent column having intermediate ports or nodes. Thus, we will describe an adsorbent column having (N - 1) intermediate nodes (for communication to variable volume spaces, feed introduction, or branching of the flow path) as a series of N adsorbent beds in a flow path. Multiple beds connected in parallel between the same nodes of the flow path are taken here as a single bed.

The working space of the apparatus includes a plurality of variable volume spaces communicating with the ends of the flow path and with some or all intermediate nodes of the flow path. The volumes of these spaces are cyclically changed at the same cyclic frequency by cyclic volume displacement means, coordinated to establish a phase relation between the spaces along the flow path. A first space 30 whose volume is changed by a first cyclic volume displacement means, provided as piston 31 reciprocating in cylinder 32, communicates with the first

end 12 of the flow path by conduit 33. An optional flow distribution means, here provided as a flow distribution screen 34 at the entrance of conduit 33 into first space 30, serves to establish substantial transverse uniformity of flow in the first space with respect to movements of piston 31, so that flow entering the first space 30 from conduit 33 is stratified over piston 31 with minimal mixing, and thus the gas withdrawn from the first end of the flow path and stored in the first space over part of each cycle will return to the first end of the flow path from the first space with minimal disturbance of any concentration gradient that was in that gas along the flow path. By preserving the concentration gradient in the flow path with minimal mixing as that gas is carried into and out of the first space, the quality of the first product may be enhanced, and more effective purging of the first adsorbent bed 15 by the gas stored in the first space 30 will be achieved.

The flow distribution means may include configuring the cylinder 32 to have a small diameter and a long stroke, to reduce the opportunity for transverse mixing except in the cylinder wall boundary layer; or else subdividing piston 31 and cylinder 32 into a plurality of smaller cylinders or compartments in parallel, between which transverse mixing is prevented. If the cylinder and adsorbent bed diameters are designed to be equal, the adsorbent bed may be mounted coaxially at the entrance of the cylinder to provide uniform transverse flow distribution, as illustrated in Fig. 5 below.

Similarly, second space 35 whose volume is changed by a second volume displacement means provided as piston 36 reciprocating in cylinder 37 communicates with the second end 13 of the flow path by conduit 38, which enters the second space 35 through a flow distribution screen serving as optional flow distribution means 39. Again,

the flow distribution means serves to preserve the concentration gradient in the flow path as gas flows into and back from the second space, thus enhancing the purity of the second product and the effectiveness by which gas stored in the second space 35 purges second adsorbent bed 16.

A first intermediate space 40 whose volume is changed by a first intermediate volume displacement means, provided as piston 41 reciprocating in cylinder 42, communicates through optional flow distribution means 43 and conduit 44 to first intermediate node 20 of the flow path. A second intermediate space 45, whose volume is changed by a second intermediate volume displacement means provided as piston 46 reciprocating in cylinder 47, communicates through an optional flow distribution means and conduit 48 to third intermediate node 22 of the flow path. A third intermediate space 49, whose volume is changed by a third intermediate volume displacement means provided as piston 50 reciprocating in cylinder 51, communicates through an optional flow distribution means and conduit 53 to the third intermediate node 24 of the flow path.

In operation of the apparatus, gas mixture is withdrawn from an intermediate node of the flow path into an intermediate space which is expanding, and is subsequently returned to the same intermediate node of the flow path by contraction of that intermediate space. While the purpose of the apparatus is to establish a concentration gradient between first and second components along the flow path, detrimental mixing events at the intermediate nodes can occur, because of mixing both in the intermediate spaces of gas mixture which departed the flow path at varying concentration, and at the intermediate node of the gas mixture being returned to the flow path with gas mixture of a different concentration already in the flow path. Such mixing

events will disturb the concentration gradient; but their effects can be minimized by use of flow distribution means in each intermediate space to miminize mixing, and by optimal phasing of the reciprocation of the pistons changing the volume of intermediate spaces so that gas returning to the flow path from an intermediate space will blend with gas mixture of substantially the same concentration already in the flow path.

Pistons 31, 36, 41, 46 and 50 are operated respectively by drive means 54, 55, 56, 57 and 58, which are coordinated by a displacement control means 59, so as to change the total volume of the working space cyclically to change the working pressure between first and second pressures, and to generate flow in the flow path from its second end to its first end when the pressure is substantially the first pressure, and to generate flow in the flow path directed from its first end to its second end when the pressure is substantialy the second pressure.

Each cyclic volume displacement means includes a cylinder containing a reciprocating piston, sealed by a piston seal means composed of a self-lubricating material such as PTFE, which may be coupled to its drive means by a piston rod and other connecting linkage as well known in the art. Reciprocating diaphagms or bellows could equivalently be used instead of pistons.

Apparatus 10 has a feed supply means including a feed supply valve 60 communicating by conduit 61 to the first intermediate node 20 of the flow path, for admitting a feed gas mixture containing first and second components to the working space. A first product enriched in the first component is withdrawn from the working space by a first product delivery means including a first product delivery valve 62 communicating by conduit 63 to the

first end 12 of the flow path, and also including a first product composition sensor 64. A second product enriched in the second component is withdrawn from the working space by second product delivery means including second product delivery valve 65 communicating to the second end 13 of the flow path by conduit 66, and also including second product composition sensor 67. A valve control means 70 is provided to control the timing and flows of feed supply valve, and the first and second product delivery valves. In particular, valve control means 70 is responsive to the first product composition sensor 64 to adjust the flow through first product delivery valve 62, and is responsive to the second product composition sensor 67 to adjust the flow through second product delivery valve 65, so as to achieve high concentration and recovery of both the first component in the first product and the second component in the second product.

The apparatus 10 with four adsorbent beds is intended to separate feed mixtures in which the first component is a large majority component, and the second component is a small minority or even trace component. The first adsorbent bed 15 serves to purify the already highly concentrated first component into the first product, while three adsorbent beds 21, 23 and 16 in series are used to concentrate the initially dilute second component by a large concentration ratio into the second product.

For concentrating a trace second component to a high degree, the principle of the invention is to compound a series of successively smaller adsorbent beds in series, each adsorbent bed in sequence from the first intermediate node 20 to the second end 13 of the flow path multiplying the concentration of the second component to the next intermediate node, so that the final concentration ratio of the second component between the feed and second product is the product of the

concentration ratios achieved by all the adsorbent beds between the feed injection point at the first intermediate node and the second end of the flow path. Adsorbent beds 21, 23 and 16 are stepped downward to smaller cross-sections in that order, commensurate with the smaller total flows necessary in the flow path as the second component becomes more concentrated and the volume of first component diluting the gas mixture becomes smaller. The swept volumes of the spaces 45, 49 and 35 are sized in approximate correspondence with the steps in adsorbent bed cross-section at each intermediate node, so as to maintain approximately similar velocity amplitude and phase in each of the adsorbent beds. In effect, adsorbent beds 21, 23 and 16 provide the function of a single long adsorbent column concentrating the second component, with the stepping down of cross-section effectively tapering the overall column in correspondence to the ascending concentration of the minority component of the feed, and with variable volume spaces communicating with discrete intermediate nodes to maintain the correct coordination of flow with pressure despite the tapering of the column.

In operation of the apparatus 10, all variable volume spaces of the working space are cyclically changed at the same frequency, but the first space 30 and second space 35 will be changed with a phase relation such that the second space is expanding while the first space is contracting while the working pressure is substantially the second pressure, and the first space is expanding while the second space is contracting while the pressure is substantially the first pressure. The cyclic volume variations in the intermediate spaces may be in phase with those of the second space, or may be phased intermediately between the phases of volume variations in the first and second spaces. Preferably, the phase of spaces 30, 40, 45, 49 and 35 will change monotonically

between the first and second ends of the flow path, so that the phase relation between working pressure (or selective adsorption and desorption responding to pressure changes) and the reversing flow in the flow path will be similar in all adsorbent beds, thus using the intermediate spaces to compensate undesirable phase shifts due to compressibility effects in the long total adsorbent column between first and second ends of the flow path.

In most applications for extraction of a small minority or trace component from a majority or carrier component, the minority second component is more readily adsorbed than the majority first component. Then, volume changes in the first space will have a leading phase with respect to volume changes in the intermediate spaces and the second space, so that flow in the flow path is directed toward its first end when the working pressure is the first pressure which is higher in this case than the second pressure.

<u>Fig. 2</u>

An apparatus 100 has four adsorbent beds along a single flow path as in the embodiment of Fig. 1, but is simplified mechanically by providing the second space and the intermediate spaces as chambers of a stepped piston. The flow path has a first end 102 and a second end 103, communicating respectively with first product delivery valve 104 and second product delivery valve 105. The first end 102 of the flow path communicates by conduit 106 to first space 107, and the second end of the flow path 103 communicates by conduit 108 to second space 109.

From its first end 102, the flow path passes through first adsorbent bed 110 to first intermediate node 111 to which the feed supply valve 112 communicates by conduit

113. From intermediate node 111, the flow path passes directly through the first intermediate space 115, which thus may be regarded as an extension of the first intermediate node, through conduit 116 to the first intermediate adsorbent bed 117. Through adsorbent bed 117, the flow path continues to second intermediate node 118, thence through second intermediate adsorbent bed 120 to third intermediate node 121 and thence through second adsorbent bed 122 to the second end 103 of the flow path.

The second and third intermediate nodes 118 and 121 may coincide with baffles for flow redistribution, as the adsorbent column cross-section is stepped at these nodes. The second intermediate node 118 is connected by conduit 125 to second intermediate space 126, and the third intermediate node is connected by conduit 127 to third intermediate space 128.

The volume of the first space 107 is cyclically changed by a first volume displacement means 130, including piston 131 reciprocating in cylinder 132. First drive means 133 is coupled to piston 131 by piston rod 134. The volume of the second space 109, third intermediate space 128, second intermediate space 126, and first intermediate space 115 are cyclically changed in the same phase and with the same stroke by stepped piston 140 reciprocating within stepped cylinder 141, stepped piston having piston seals 145, 146, 147 and 148 to seal cylinder sections of successively smaller diameter within stepped cylinder 141.

Thus, cross-sectional areas are defined, of the second space 109 by the sealing area of seal 145, of the third intermediate space 128 by the annular area between seals 145 and 146, of the second intermediate space 126 by the annular area between seals 146 and 147, and of the first intermediate space 115 by the annular area between seals

147 and 148. Stepped piston 140 is driven by second drive means 150 through piston rod 151. Drive means 150 and 133 cooperate to establish a phase relation between volume changes in the first and second spaces, such that volume changes in the first space lead volume changes in the second space when the second component is more readily adsorbed than the first component.

Referring to Fig. 2, variable volume second intermediate space 126 communicates by conduit 125 to intermediate node 118 of the flow path between adsorbent beds 117 and 120. With the second component more readily adsorbed than the first component, the first pressure is higher than the second pressure. Volume changes in second space 109 and in second intermediate space 126 (which are in phase because of the stepped piston configuration) lag volume changes in first space 107. Thus, space 126 expands when the working pressure is relatively low, and contracts when the working pressure is relatively high. The gas mixture contacting the adsorbent beds is relatively enriched in the second component when the pressure is low, and relatively depleted in the second component when the pressure is elevated. Thus, gas mixture flowing into space 126 will be relatively enriched in the second component owing to the typically lower pressure, while this gas will be returned to intermediate node 118 during an interval of higher pressure when the gas in the flow path then flowing from adsorbent bed 120 to bed 117 will be less concentrated in the second component during much of this interval. Thus, some undesirable mixing of relatively enriched gas from space 126 into less enriched gas already in the flow path at node 118 will occur in this embodiment. Similarly, mixing will occur in the first intermediate space 115, through which the flow path passes between adsorbent beds 110 and 117.

One approach for compensating such mixing effects is to connect an intermediate variable volume space to a pair of intermediate nodes on either side of a short adsorbent bed segment in the flow path between longer adsorbent bed segments, with check valves in the connections so that the flow entering the intermediate space during its expansion stroke comes from only one of the intermediate nodes, while flow leaving the intermediate space returns only to the other intermediate node. By returning the flow from the intermediate space to a different point of the total adsorbent column than where it was extracted, flexibility is provided to allow for changes in local composition of the interstitial gas in the adsorbent column during different phases of the cycle, and to minimize adverse mixing effects.

Example No. 1

An application for this invention of potential future importance is the extraction and concentration of trace levels of hydrogen isotopes including tritium from helium. The tritium would be generated in the lithium blanket surrounding a fusion reactor, and flushed from this blanket by a helium purge stream. The tritium must be extracted from the helium, concentrated and purified before use as reactor fuel.

An experimental apparatus as depicted in Fig. 1 and in the specific arrangement of Fig. 2 was assembled with adjustable phase between the first and second spaces, and with the intermediate spaces all reciprocating in phase with the second space. Pistons sealed by spring-loaded PTFE cup seals were used as the cyclic volume displacement means. With typical operating piston strokes, the swept volumes of the spaces were 300 cc for the first space, 130 cc for the first intermediate space, 97 cc for the second intermediate space, 47 cc for the

third intermediate space, and 30 cc for the second space. Adsorbent bed volumes were 59.7 cc for the first adsorbent bed, 41.5 cc for the first intermediate adsorbent bed, 26.5 cc for the second intermediate adsorbent bed, and 14.9 cc for the second adsorbent bed.

The apparatus was operated with all adsorbent beds cooled by dry ice to a working temperature of about 195 K, at which hydrogen is much more readily adsorbed than helium over common adsorbents. Zeolite 10X adsorbent was used. The working pressure cycled between the feed pressure of approximately 1.5 atm absolute and the helium product delivery pressure of approximately 3.5 atm absolute, at an experimental operating cycle frequency of 5 cycles/min. The phase of volume changes in the second space was typically 90° leading volume changes in the first space.

The feed gas mixture was helium containing 0.1 % ordinary hydrogen, supplied at a fixed nominal flow of 250 cc/min. The ratio of first and second product flows was controlled by timing of solenoid valves serving as product delivery valves, and by adjusting a needle valve as part of the second product delivery means to control the second product flow rate directly. After the apparatus was started with clean adsorbent beds, it was found that pure helium could be delivered immediately as the first product, but that several hours of operation were necessary to accumulate sufficient hydrogen in the adsorbent beds and spaces between the first intermediate node and the second end of the flow path, before a concentrated hydrogen product could be delivered as the second product. The time required to charge the apparatus with hydrogen was reduced by operating during this period with no second product delivery flow. However, some second product delivery flow was desirable when the apparatus needed to be purged of any residual

air.

Once the apparatus was charged with hydrogen reaching a desired concentration in the second space, it was found that the second product could be withdrawn and stable conditions established by suitable adjustment of the product delivery valves. Hydrogen concentration of 90% was obtained from the 0.1 % feed, when the flow ratio of second product to first product flow was 0.001, equal to the feed concentration ratio of second to first component. Since hydrogen recovery was 90%, by mass balance the helium stream was incompletely purified although the trace hydrogen was not detectable in the gas chromatograph.

When the ratio of second product to first product was increased to 0.003, or three times the feed concentration ratio of second to first component, hydrogen purity in the second product was measured at 34%, indicating 100% recovery of hydrogen and by mass balance complete purification of the helium first product.

Fig. 3

Embodiment 500 of the invention has N = 3 for each of two working spaces, and four variable volume spaces along each flow path. The volume of each variable volume space along a flow path is changed by a hydraulic volume displacement means, with the phase shifts established by hydraulic impedance between the liquid displacement chambers. A reversing liquid pump generates oscillating liquid flow between the groups of liquid displacement chambers associated with each flow path.

Apparatus 500 has a left working space with a first end of the left flow path 501 communicating with left first space 502, left first product delivery valve 503, and

left first adsorbent bed 504. The left flow path passes through first adsorbent bed 504 to left first intermediate node 505, communicating with left first intermediate space 506, left feed supply valve 507 and left intermediate adsorbent bed 508. The flow path continues through left intermediate adsorbent bed 508 to left second intermediate node 509 communicating with left second intermediate space 510 and left second adsorbent bed 514, and through adsorbent bed 514 to second end 515 of the left flow path communicating with left second space 516 and left second product delivery valve 517.

Similarly, a right working space has a first end of the right flow path 521 communicating with right first space 522, right first product delivery valve 523, and right first adsorbent bed 524. The right flow path passes through first adsorbent bed 524 to right first intermediate node 525, communicating with right first intermediate space 526, right feed supply valve 527 and right intermediate adsorbent bed 528. The flow path continues through right intermediate adsorbent bed 528 to right second intermediate node 529 communicating with right second intermediate space 530 and right second adsorbent bed 534, and through adsorbent bed 534 to second end 535 of the right flow path communicating with right second space 536 and right second product delivery valve 537.

In embodiment 500, each of the variable volume spaces 502, 506, 510, 516, 522, 526, 530 and 536 is cyclically changed by a liquid displaced bellows, each of which forms a hydraulic volume displacement means. The bellows, or equivalent diaphragm cr piston, must be leak-tight to prevent ingress of the liquid or its vapour into the working spaces. A reversing pump means 540 is provided to displace liquid back and forth betwen the hydraulic volume displacement means on the left and right

sides of the apparatus.

Pump 540 generates reversing flow to the left side of the apparatus through left conduit 550, communicating from pump 540 to a left first liquid displacement chamber 551 displacing bellows 552 to vary the volume of space 502, and to conduit 555. Conduit 555 communicates through left first hydraulic phase-shifting means 556 to a left first intermediate liquid displacement chamber 559 displacing bellows 560 into space 506, and to conduit 561. Conduit 561 communicates through left second hydraulic phase-shifting means 562 to left second intermediate liquid displacement chamber 565 displacing bellows 566 into space 510, and to conduit 567. Conduit 567 communicates through left third phase-shifting means 568 to left second liquid displacement chamber 569 displacing bellows 570 into left second space 516.

Similarly, pump 540 transfers liquid between left conduit 550 to right conduit 580, communicating from pump 540 to a right first liquid displacement chamber 581 displacing bellows 582 to vary the volume of space 522, and to conduit 585. Conduit 585 communciates through right first hydraulic phase-shifting means 586 to a right first intermediate liquid displacement chamber 589 displacing bellows 590 into space 526, and to conduit 591. Conduit 591 communicates through right second hydraulic phase-shifting means 592 to right second intermediate liquid displacement chamber 595 displacing bellows 596 into space 530, and to conduit 596. Conduit 596 communicates through right third hydraulic phase-shifting means 597 to right second liquid displacement chamber 598, displacing bellows 599 into right second space 536.

With utmost simplicity, the hydraulic phase-shifting means are provided by the hydraulic inertial and frictional impedance of the conduits described as

communicating through such means. By providing cumulatively greater inertia in the conduits further from the pump, a phase shift will be generated between the spaces in each flow path, such that the first space has leading phase, the second space has lagging phase, and the intermediate spaces have sequentially intermediate phases between the first and second phases. Inertia in the conduits is increased by increasing conduit length or reducing conduit diameter. From Fig. 3, the above phase relationships are apparent since the conduit length between pump and each variable volume space is minimal for the first spaces and increases toward the second spaces. The phase shift between the spaces in each flow path may be increased by incorporating a spring restoring force in the bellows (as will be the case with metal bellows), and suitably designing the spring stiffness of each bellows, so that at the operating cyclic frequency, the impedance of the hydraulic volume displacement means associated with the first space in a flow path is spring-dominated, while the impedance of the hydraulic volume displacement means with associated liquid conduits is increasingly inertia-dominated progressing to the second space. The phase-shifting means may include throttle or flow control valves or other means such as flow metering pumps for precise control and adjustment.

In embodiment 500, the apparatus is operated entirely apart from valve actuation by pump 540. If the potential energy stored in the gas working spaces and by deflection of the bellows is approximately equal to the kinetic energy stored in the liquid conduits and pump, the apparatus will be operating at approximately its resonant frequency, and power demand peaks will be minimized.

Fig. 4

A gas separator according to the invention in preceding embodiments can accept a binary mixture of two components or fractions, with a feed concentration ratio of the first to the second component, and can separate those components with high purity and recovery when the ratio of first product to second product is established under steady state conditions to be approximately equal to the feed concentration ratio. Perfect simultaneous purification of both products is most difficult, although this objective may be approached more closely than in prior art separation systems. The first product will tend to have higher purity in the first component when the ratio of the first product to the second product is somewhat less than the feed concentration ratio, and the second product will tend to have higher purity in the second component when the ratio of the first to second products is somewhat greater than the feed concentration ratio. While operating with the ratio of first to second products very close to the feed concentration ratio, very high purity of both products may be achieved by operating with low feed flow rate.

In order to achieve high productivity by operating with high feed flow rate, a first stage gas separator 601 in Fig. 4 is operated with the ratio of its first product to its second product considerably <u>less</u> than the feed concentration ratio of the first to second component. When the second component feed concentration is low (i.e. of the order of 1% or less), the ratio of first to second product may be for example about half the feed concentration ratio. Then, the first product will be highly purified with about 99% recovery, while the second component in the second product will be concentrated to about 50%. The second product of the first separator is then used as second stage feed gas mixture having a

second stage feed concentration ratio to a second stage gas separator 602, which operates with its ratio of first product to second product larger than the second stage feed concentration ratio of second stage first product to second product. Now the second product of the second stage separator is highly purified, while the second stage first product is depleted in the second component relative to second stage feed but only incompletely purified in the first component. The second stage first product is then recycled to an intermediate node of the first stage separator 601, as a supplementary feed to the first stage. The overall apparatus comprising a cascade of first stage separator 601 and second stage separator 602 is thus able to purify both feed components to an extremely high degree, while operating at high productivity of the first stage which typically is much larger than the first stage. Hence, total adsorbent inventory and physical size of the cascaded apparatus may be reduced compared to a single apparatus (such as Fig. 1) operating at low feed flow rate in order to approach high purity of both products without cascading to a second stage separator.

In the example of Fig. 4, first stage separator 601 has N = 3 in a flow path with first end 605, first adsorbent bed 606, first intermediate node 607, intermediate adsorbent bed 608, second intermediate node 609, second adsorbent bed 610 and second end of the flow path 611. Variable volume spaces, with associated cyclic volume displacement means operating at a cyclic frequency, communicate with the ends of the flow path and to some or all intermediate nodes. The feed gas mixture is introduced by feed supply valve 615 to first intermediate node 607. Purified first component is withdrawn through first product delivery valve 616, which is controlled by valve controller 617 sensing purity of the first component at the first end 605 of the flow path, so that

first product is only released by valve 616 when its purity is acceptable to controller 617. The second product of the first stage is concentrated in the second component, and delivered from the second end 611 of the flow path through first stage second product valve 620 communicating with conduit 621 and gas storage buffer volume 622.

Second stage separator 602 has a flow path with a first end 630, a first adsorbent bed 631, a first intermediate node 632, an intermediate adsorbent bed 633, a second intermediate node 634, a second adsorbent bed 635, and a second end 636 of the flow path. Variable volume spaces with associated cyclic volume displacement means operating at a cyclic frequency communicate with the ends and intermediate nodes of the flow path. Second stage feed is introduced to first intermediate node 632 by feed supply valve 640 which receives first stage second product gas from conduit 621 and buffer volume 622. Purified second component is withdrawn from second end 636 of the flow path by second product delivery valve 645, which is controlled by valve controller 646 sensing purity of the second component at the second end 636 of the flow path, so that second product is only released by second product delivery valve 645 when the second product purity is acceptable to controller 646. The second stage first product is discharged from the first end 630 of the flow path by second stage first product delivery valve 650, communicating to conduit 651 and buffer volume 652 which in turn communicate with a supplemental feed supply valve 653 connected to intermediate node 609 of the first stage flow path, providing means to recycle the second stage first product to an intermediate node of the first flow stage path. Thus, the second component in the first stage second product is further purified by the second stage, while the first component in the first stage second product is concentrated by the second stage and

recycled to the first stage for concentration and purification.

The cascaded apparatus of Fig. 4 should be operated with suitable adsorbent bed sizing and flow rates, such that the gas mixture concentrations referred to the same pressure are the same at second end 620 and node 632, and first end 650 and node 609. Then the gas concentration in the flow paths will change monotonically from pure first component at the first stage first end 605, with increasing second component concentration sequentially at nodes 607, 609, 632, and 634 until the second component is pure at second stage second end 636.

A further generalization applies in applications where feed gas mixtures containing the first and second components in different ratios are available to the same apparatus. The feed gas mixture admitted to the feed supply valve 615 typically is rich in the first component, and contains only a small concentration of the second component. If a second feed gas mixture rich in the second component, and only containing a small concentration of the first component, is also available, that feed gas mixture should be introduced to the flow path at an intermediate node close to the second end of the flow path, so that feed gas mixture introduced to the flow path is supplied at a location and cycle time when the local concentration in the flow path has about the same concentration as the feed gas. To illustrate this generalization, which is applicable to single or cascaded gas separators according to the invention, a supplementary feed gas supply valve 660 is shown communicating to second intermediate node 634 of the second stage flow path. A feed gas mixture that is already nearly purified in the second component could be introduced by supplementary feed valve 660.

Fig. 5

Apparatus 700 is configured for separating the three components of a ternary gas mixture, and thus has a branched flow path to provide three flow path ends to which a product component can be concentrated. The feed gas mixture contains first, second and third components which will be separated into first, second and third products respectively. One of the first or second components is more readily adsorbed than the other, and the third component is intermediate in readiness of adsorption between the first and second component. Another feature illustrated in Fig. 5, which may be applied independently to other embodiments, is a further branching of the flow path at the first intermediate node so that the feed is introduced through a feed adsorbent bed within the working space, so that an undesired strongly adsorbed gas component or vapour (in addition to the two or three components to be separated as products) can be captured and eliminated before the gas mixture reaches the first intermediate node.

The apparatus 700 has a first end of the flow path 701 communicating with first space 702, first adsorbent bed 703, and first product delivery valve 704. The flow path passes through adsorbent bed 703 to first intermediate node 705, at which the feed gas mixture (less any strongly adsorbed vapour component) is introduced to the flow path. The flow path passes from first intermediate node 705 through first intermediate adsorbent bed 706 to second intermediate node 707, at which the flow path branches into a first branch and a second branch.

The first flow path branch continues from second intermediate node 707 through second intermediate adsorbent bed 710 to third intermediate node 711 communicating with a second intermediate space 712 and

second adsorbent bed 713, through which the second flow path continues to second flow path end 714. Second flow path end 714 communicates with second space 715 and second product delivery valve 716. The second flow path branch continues from second intermediate node 707 through third adsorbent bed 720 to third flow path end 721, communicating with third space 722 and a third product delivery valve 723.

The first component is either more or less readily adsorbed than the second and third components. The principle of the present apparatus in separating a ternary mixture is to establish a concentration gradient of the first component along the flow path, so that the gas at first flow path end 701 is substantially pure first component, at node 705 is more or less feed gas mixture concentration, and at node 707 is a mixture of the second and third components with substantially no first component. The flow in the flow path is coordinated with pressure changes such that gas contacting the adsorbent beds in the flow path is relatively enriched in the first component when flowing toward the first flow path end, and relatively depleted in the first component when flowing toward the second and third flow path ends. Thus, the first component is inhibited from passing through adsorbent bed 706 from node 705 to reach node 707 branching to the second and third flow path branches. The flow in the second and third flow path branches is then coordinated with changes in working pressure, so that there is net flow from the second flow path end to the third flow path end when the gas mixture contacting the adsorbent beds in the second and third flow path branches is relatively enriched in the third component, and there is net flow from the third flow path end to the second flow path end when the gas contacting the adsorbent beds in the second and third flow path branches is relatively enriched in the second

component.

The above specified flow and pressure relationships can be achieved by operating the volume displacement means associated with the first, second and third spaces, so that the first and second spaces cycle in volume with a phase difference to achieve separation between the first and second components, one of which is more readily adsorbed than the other; and the third space cycles in volume at a phase intermediate between the first and second spaces since the third component has intermediate readiness of adsorption between the first and second components.

While the feed gas mixture could here be introduced by a feed supply valve directly to the first intermediate node as described for other embodiments, another optional feature is illustrated which enables removal of a strongly adsorbed vapour (more generally, a third component of the feed gas mixture more readily adsorbed than the first or second components) before the feed gas reaches the main flow path. A feed adsorbent bed 730 communicates with first intermediate node 705, and forms a feed flow path branch which passes from node 705 through feed adsorbent bed 730 and terminates in a feed flow path end 731, communicating with feed supply valve 732 (or other feed supply means) and an exhaust valve 733. Feed gas mixture containing the strongly adsorbed vapour component is introduced to feed flow path end 731 during an interval of relatively high working pressure when the feed supply valve 732 is opened, and feed gas mixture then flows to intermediate node 705 and into the main flow path, while the strongly adsorbed vapour component is retained in adsorbent bed 730 near feed end 731 without penetrating to intermediate node 705. During the subsequent interval of relatively low working pressure, exhaust valve 733 is opened to permit some gas

mixture in the flow path to enter adsorbent bed 730 from node 705, and flow through adsorbent bed 730 and out through exhaust valve 733 to purge the strongly adsorbed vapour which was adsorbed at higher pressure and is desorbed at lower pressure. Thus, means is provided to remove a strongly adsorbed vapour which will thus not be a product of the separation, with the penalty of using some of the gas mixture containing desirable products as purge gas which will not be recovered in this apparatus. This feature may be added to any embodiment of this invention, whether used in separation of gas mixtures containing two or three (as in Fig. 5) components in addition to the strongly adsorbed vapour, and is particularly useful in air separation to remove water vapour so that dry nitrogen and oxygen products may be separated without deactivation of a zeolite adsorbent by water vapour.

In Fig. 5, each of the first, second and third adsorbent beds 703, 713 and 720 has a similar cross-section to, and is mounted coaxially to, the corresponding first, second and third space 702, 715 and 722; so that gas flows between the adsorbent beds and the spaces at each flow path end with substantially uniform velocity transverse to the flow path. Coaxial mounting of the adsorbent bed and variable volume space having similar cross-section at a flow path end is thus means to establish substantially uniform flow in the variable volume space, so as to maintain substantial axial stratification of the gas within the variable volume space for improved purging effectiveness and product purity.

<u>Example No. 2</u>

The feed gas to apparatus 700 is air, from which purified oxygen, nitrogen and argon are desired products. Conventional pressure swing adsorption systems using

zeolite adsorbents over which nitrogen is more readily adsorbed than oxygen and argon cannot produce better than 95% purity oxgyen because of argon concentration into the oxygen product, and cannot readily concentrate nitrogen unless water vapour has previously been removed from the feed. Conventional systems using a kinetic separation over carbon molecular sieves, over which oxygen is more rapidly adsorbed than nitrogen and argon, are useful in inert gas generation but are not easily optimized for production of pure oxygen.

In this example, the adsorbent in feed adsorbent bed 730 is a dessicant such as alumina gel. The adsorbent in beds 703 and 706 is a zeolite molecular sieve such as 10X, more readily adsorbing nitrogen than oxygen or argon. The adsorbent in beds 710, 713 and 720 will be selective between oxygen and argon, and may be a carbon molecular sieve or a zeolite. The apparatus is operated with a leading phase of volume changes on second space 715, a lagging phase of volume changes in first space 702, and an intermediate phase of volume changes in third space 722. Thus, water vapour in the feed air is removed before the feed gas reaches first node 705. Nitrogen is concentrated as the first product to the first flow path end 701, and is removed from gas mixture passing from adsorbent bed 706 to node 707. Argon is concentrated to the second flow path end 74, while purified oxygen is delivered at third flow path end 721.

Example No. 3

A steam methane reforming reactor delivers a syngas mixture containing (after water removal) hydrogen, carbon dioxide, carbon monoxide and unreacted methane, with a typical composition as follows: H_2, 74%; CO, 18%; CO_2, 6%; and CH_4, 2%. Over typical zeolite or charcoal adsorbents, carbon dioxide may be defined as a first

component which is strongly adsorbed, and hydrogen may be defined as a first component which is weakly adsorbed. The remaining fraction of CO and CH_4 may be defined as a third component which under increase of pressure is more readily adsorbed than the less readily adsorbed of the first and second components, and less readily adsorbed than the more readily adsorbed of the first and second components.

The above syngas mixture is introduced to the first intermediate node of embodiment 700, which is operated so that volume changes in first space 702 have a lagging phase with repect to volume changes in second space 715, while volume changes in third space 722 have an intermediate phase between the first and second spaces. A first product of purified carbon dioxide is delivered at the lower cycle pressure from first product delivery valve 704, and a second product of purified hydrogen is delivered from second product delivery valve 716. The third product containing carbon monoxide and methane (and some hydrogen and carbon dioxide) is delivered from third product delivery valve 723 at preferably the higher cycle pressure, and this third product is then recycled directly to the steam reforming reactor. Consequently the steam reforming reactor is subjected to a back pressure of carbon monoxide, suppressing further production of CO.

In the absence of any purge to remove inert components, the gas separator of this invention forces the steam reforming process to achieve high yield of hydrogen and byproduct carbon dioxide, with greatly improved selectivity and complete conversicn of feedstock. Water gas shift reactors conventionally used to convert a fraction of the carbon monoxide can be eliminated, since carbon monoxide formation is inhibited. Hence the feed gas mixture of syngas from the steam reforming reactor

can be provided to the gas separation apparatus without an intermediate step of processing in a water gas shift reactor. The hydrogen losses to low grade fuel from the purge stream of conventional pressure swing adsorption hydrogen purification plants (typically only recovering 85% of the hydrogen in the syngas) are avoided. Most importantly, the endothermic heat of reaction for steam methane reforming is considerably reduced when CO_2 is the only carbon oxide produced, so the process requirement for high grade heat and fuel may be reduced for much improved overall efficiency.

Several simplifications of the apparatus of Fig. 11 are appropriate for syngas separation. Since hydrogen is the majority component, intermediate space 712 may be eliminated, and adsorbent bed segments 710 and 713 may be combined into one bed. A hydrophobic adsorbent may be used in adsorbent bed 703 to avoid deactivation by water vapour. The second end of the flow path may be heated relative to the first end, so that the process is in part thermally powered. Nitrogen present in the syngas mixture may be separated into the first product with the hydrogen (as desired for ammonia synthesis), or into the third product of which a purge fraction may then be used as reforming furnace fuel.

This example shows that the invention relates to chemical reaction processes in which the reactor effluent is a gas phase mixture including the three fractions of a first product, a second product, and a third fraction of components which are incompletely converted to the products. The invention here provides an adsorptive gas separation apparatus for separating the said three fractions, so that the third fraction can be recycled to the reactor for improved yield of the first and second products, thus overcoming reaction equilbrium constraints.

INDUSTRIAL APPLICABILITY

As illustrated by the embodiments and examples described above, the present invention achieves substantial advances in separation of binary or multicomponent gas mixtures, including unique capabilities for simultaneous extraction and concentration of a trace component, and for separation of three product fractions from a multicomponent gas mixture.

It will be understood that the different aspects of the present invention may be expressed with much diversity and in many further combinations, under the scope of the following claims.

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1. A process for separating a feed gas mixture containing first and second components, the feed gas mixture having a feed concentration ratio between the first and second components, and one of the first and second components being more readily adsorbed under increase of pressure relative to the other component which is less readily adsorbed under increase of pressure over an adsorbent material, such that a gas mixture of the first and second components contacting the adsorbent material is relatively enriched in the first component at a first pressure and relatively enriched in the second component at a second pressure when the pressure is cycled between the first and second pressures at a cyclic frequency; providing for the process a flow path through a first adsorbent bed segment and a second adsorbent bed segment in a working space within which the gas mixture has a working pressure, with the adsorbent material contacting the flow path in the adsorbent bed-segments, and the flow path having first and second ends and a first intermediate node in the flow path between adjacent adsorbent bed segments, so that the flow path passes through the first adsorbent bed segment in the flow path between the first end of the flow path and the first intermediate node, and through the second adsorbent bed segment in the flow path to the second end of the flow path; providing within the working space a first space communicating with the first end of the flow path, a second space communicating with the second end of the flow path, and a third space communicating with the first intermediate node; performing volume changes with an amplitude and phase at the cyclic frequency in the first, second and third spaces; and establishing a phase difference between the volume changes of the first and second space; and the process including the cyclically repeated steps at the cyclic frequency and in some sequence of:

(a) introducing the feed gas mixture to the flow path at the first intermediate node,

(b) changing the volume of the first space, the second space and the third space, and establishing an amplitude and phase of the volume changes at the cyclic frequency in each of the first space, second space and third space, so as to change the volume of the working space in order to change the working pressure between the first pressure and the second pressure,

(c) while the working pressure is at the first pressure, so that the gas mixture contacting the adsorbent bed segment is relatively enriched in the first component, expanding the first space while contracting the second space; so as to generate flow in the flow path directed from the second space to the first space, to accumulate within the first space some gas enriched in the first component which has flowed into the first space from the first adsorbent bed segment, and also to purge the second adsorbent bed segment with gas which was in the second space,

(d) changing the volume of the working space in order to change the working pressure from the first pressure to the second pressure,

(e) while the working pressure is at the second pressure, so that the gas mixture contracting the adsorbent bed segments is relatively enriched in the second component, expanding the second space while contracting the first space; so as to generate flow in the flow path directed from the first space to the second space, to accumulate within the second space some gas enriched in the second component which has flowed into the second space from the second adsorbent bed segment, and also to purge the first adsorbent bed segment with gas which was in the first space,

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(f) changing the volume of the working space in order to change the working pressure from the second pressure to the first pressure,

(g) withdrawing from adjacent the first end of the flow path a first product gas enriched in the first component,

(h) withdrawing from adjacent the second end of the flow path a second product gas enriched in the second component,

(i) controlling the withdrawal of the first and second product gases, so as to achieve high concentration and recovery of both the first component in the first product and the second component in the second product.

2. The process of claim 1, further providing at least one intermediate node in the flow path in addition to the first intermediate node, and an intermediate adsorbent bed segment between each adjacent pair of intermediate nodes, so that the number "N" of adsorbent bed segments is at least three.

3. The process of claim 1, in which the feed gas mixture contains a third component which under increase of pressure is more readily adsorbed than the first and second components, and the process is further characterized by:

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(a) extending a feed flow path branch from the first intermediate node of the flow path, with the feed flow path branch terminating in a feed flow path end,

(b) providing the additional adsorbent bed segment as a feed adsorbent bed segment in the feed flow path branch between the first intermediate node and the feed flow path end,

(c) introducing the feed gas mixture to the feed flow path end when the working pressure is at the higher of the first and second pressures, and

(d) exhausting gas enriched in the third component from the feed flow path end when the working pressure is at the lower of the first and second pressures.

4. The process of claim 1, further characterized by:

(a) providing at least one intermediate node in the flow path in addition to the said first intermediate node, and

(b) providing an intermediate adsorbent bed segment in the flow path between each pair of intermediate nodes, so that the said additional adsorbent bed is an intermediate adsorbent bed in the flow path, and

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5. The process of claim 4, further characterized by:

   (a) providing an intermediate space communicating with an intermediate node, and

   (b) performing volume changes in the intermediate space at the cyclic frequency and with a phase relative to the volume changes in the first and second spaces.

6. The process of claim 5, further performing volume changes in an intermediate space communicating with each intermediate node except the first intermediate node.

7. The process of claim 5, further performing volume changes in an intermediate space communicating with each intermediate node including the first intermediate node.

8. The process of claim 5, further establishing the volume changes of an intermediate space to be in phase with volume changes of the first space.

9. The process of claim 5, further establishing the volume changes of an intermediate space to be in phase with volume changes of the second space.

10. The process of claim 5, further establishing the phase of volume changes of each intermediate space to be intermediate in phase between the volume changes of the first and second spaces.

11. The process of claim 1, further establishing the amplitudes of the volume changes in the first and second spaces to be in a ratio in approximate proportion to the feed concentration ratio of the first to the second component.

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12. The process of claim 5, in which the first component is a majority component and the second component is a minority component, and further providing the adsorbent beds in the flow path between the first intermediate node and the second end of the flow path in sequentially smaller sizes descending toward the second end of the flow path, so that the second adsorbent bed is smallest, and establishing the amplitude of volume changes of the second space to be smaller than the amplitude of volume changes of the first space.

13. The process of claim 12, in which the feed concentration ratio of the first component to the second component is of the approximate order of 10:1, and "N" = 3.

14. The process of claim 12, in which the feed concentration ratio of the first component to the second component is of the approximate order of 100:1, and "N" = 4.

15. The process of claim 12, in which the feed concentration ratio of the first component to the second component is of the approximate order of 1000:1, and "N" = 5.

16. The process of claim 4 in which the feed gas mixture includes a third component which under increase of pressure is more readily adsorbed than the less readily adsorbed of the first and second components, and less readily adsorbed than the more readily adsorbed of the first and second components, further characterized by:

(a) providing a second flow path branching from the first flow path from a second intermediate node between the first intermediate node and the

second end of the flow path, with the second flow path passing through a third adsorbent bed to a third flow path end,

(b) performing volume changes in a third space at the third flow path end at the cyclic frequency,

(c) coordinating volume changes of the first, second and third spaces so that the phase of volume changes in the third space is intermediate between the phase of volume changes in the first and second spaces, so as to concentrate the first component to the first flow path end, the second component to the second flow path end, and the third component to the third flow path end, and

(d) withdrawing from adjacent the third flow path end a product enriched in the third component.

17. The process of claim 1, further withdrawing the first and second products in a ratio of the first and second products less than the feed concentration ratio of the first and second components, so as to obtain a first product of enhanced purity in the first component.

18. The process of claim 17 as a first stage, and providing a similar second stage, further taking the second product of the first stage which is incompletely purified in the second component as feed gas mixture to the second stage, and withdrawing the first and second products of the second stage in a ratio less than the feed concentration ratio of the first and second components of the second stage, so as to obtain a second product of enhanced purity from the second

stage, while returning the impure first product of the second stage to an intermediate node of the flow path of the first stage; whereby operating the first and second stages as a cascade to purify the first and second components, and withdrawing highly purified first and second products from the first and second stages respectively.

19. Apparatus for separating and concentrating first and second components of a feed gas mixture, the feed gas mixture having a feed concentration ratio between the first and second components, and one of the first and second components being more readily adsorbed under increase of pressure relative to the other component which is less readily adsorbed under increase of pressure over an adsorbent material, such that a gas mixture of the first and second components contacting the adsorbent material is relatively enriched in the first component at a first pressure and relatively enriched in the second component at a second pressure when the pressure is cycled between the first and second pressures at a cyclic frequency; and the apparatus including:

(a) a working space including a flow path passing over the adsorbent material in adsorbent bed segments, with the flow path having first and second ends,

(b) a first adsorbent bed segment in the flow path, between the first end and a first intermediate node of the flow path,

(c) a second adsorbent bed segment in the flow path, and communicating with the second end of the flow path,

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(d) feed supply means for introducing the feed gas mixture to the flow at the first intermediate node,

(e) first product delivery means for withdrawing a first product enriched in the first component from adjacent the first end of the flow path,

(f) second product delivery means for withdrawing a second product enriched in the second component from adjacent the second end of the flow path,

(g) first cyclic volume displacement means to change the volume of a first space within the working space and communicating with the first end of the flow path,

(h) second cyclic volume displacement means to change the volume of a second space within the working space and communicating with the second end of the flow path,

(i) means to operate the first and second volume displacement means at the cyclic frequency, so as to change the working pressure between the first and second pressures,

(j) means to coordinate the relative phase of the volume displacement means, to provide a phase difference between the first and second volume displacement means so as to generate flow in the flow path directed from the second space to the first space while the working pressure is at the first pressure, and also to generate flow in the flow path

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directed from the first space to the second space while the working pressure is at the second pressure,

(k) means for expanding the first space and contracting the second space while the working pressure is at the first pressure, so as to accumulate within the first space some gas enriched in the first component which has flowed into the first space from the first adsorbent bed, and also to purge the second adsorbent bed with gas which was in the second space,

(l) means for expanding the second space and contracting the first space while the working pressure is at the second pressure, so as to accumulate within the second space some gas enriched in the second component which has flowed into the second space from the second adsorbent bed, and also to purge the first adsorbent bed with gas which was in the first space,

(m) means for controlling the withdrawal of the first and second product gases, so as to achieve high concentration and recovery of both the first component in the first product and the second component in the second product,

20. The apparatus of claim 19, further including at least one intermediate node in the flow path in addition to the first intermediate node, and an intermediate adsorbent bed segment between each adjacent pair of intermediate nodes, so that the number of adsorbent bed segments is at least three.

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21. The apparatus of claim 19, further including a feed adsorbent bed segment in a feed flow path branch extending from the first intermediate node to a feed flow path end communicating with the feed supply means and an exhaust valve, so that the feed supply means admits feed gas mixture into the feed adsorbent bed segment from the feed flow path end when the working pressure is the higher of the first and second pressures, and the exhaust valve means discharges some gas mixture from the working space when the working pressure is the lower of the first and second pressures, the gas mixture discharged by the exhaust valve being enriched in any third component of the feed gas mixture that is more readily adsorbed under increase of pressure than the first and second components, so that the gas mixture entering the flow path at the first intermediate node will be depleted in the third component.

22. The apparatus of claim 19, further including at least one intermediate node in the flow path in addition to the said first intermediate node, and including an intermediate adsorbent bed segment in the flow path between each pair of intermediate nodes.

23. The apparatus of claim 22, further including:

(a) an intermediate space communicating with an intermediate node, and

(b) an intermediate cyclic volume displacement means to change the volume of the intermediate space, and

(c) means to operate the intermediate cyclic volume

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displacement means at the cyclic frequency and with a phase relative to the first and second volume displacement means.

24. The apparatus of claim 23, with means to establish the volume changes of the intermediate space to be in phase with volume changes of the second space.

25. The apparatus of claim 19, with means to establish the phase of volume changes of the intermediate space to be intermediate in phase between the volume changes of the first and second spaces.

26. The apparatus of claim 25, in which the phase of volume changes in the first, second and the intermediate space are established by the relative impedance of hydraulic connections between hydraulic volume displacement means to cyclically change the volumes of the first, second and intermediate spaces, and hydraulic pump means generating a cyclic hydraulic flow to actuate the hydraulic volume displacement means.

27. The apparatus of claim 19, with means to determine the amplitudes of the volume changes in the first and second spaces in a ratio in approximate proportion to the feed concentration ratio of the first to the second component.

28. The apparatus of claim 19 with the flow path branched from an intermediate node so that the working space has three flow path ends including a third flow path end, and with an adsorbent bed segment in the flow path branch between the said intermediate node and the third flow path end.

29. The apparatus of claim 28, further including:

(a) at least two adsorbent bed segments in the flow path between the first end of the flow path and the said intermediate node from which the flow path is branched,

(b) a third cyclic volume displacement means to change the volume of a third space communicating to the third flow path end,

(c) means to operate the third cyclic volume displacement means at the cyclic frequency, and to coordinate the phase of volume changes in the third space to be intermediate between the phase of volume changes in the first and second spaces, and

(d) a third product delivery means communicating with the third flow path end so as to withdraw gas enriched in a third component of the feed gas mixture, the third component being more readily adsorbed under increase of pressure than the less readily adsorbed of the first and second components, and the third component being less readily adsorbed under increase of pressure than the more readily adsorbed of the first and second components.

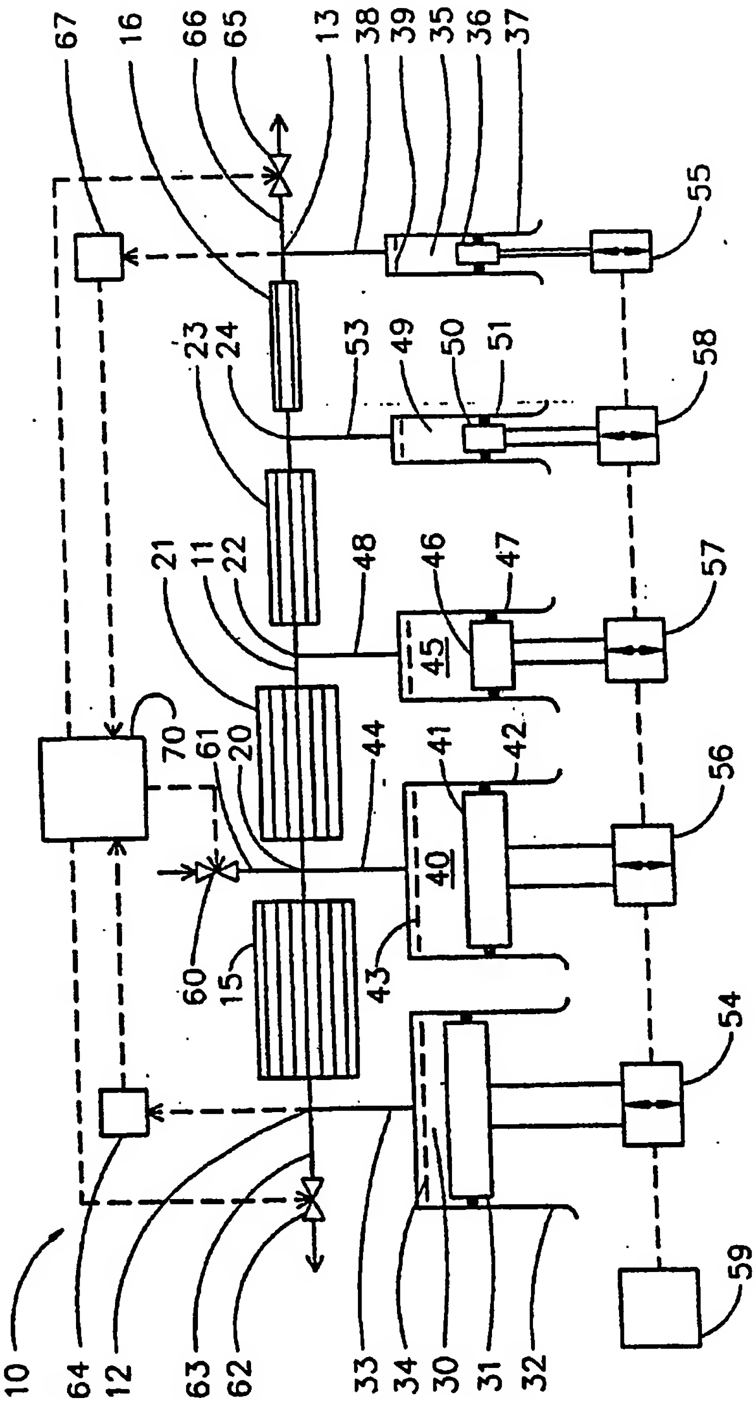
30. The process of claim 16, in which the feed gas mixture is air, the first component is nitrogen, the second component is argon, and the third component is oxygen.

31. The process of claim 16 in which the feed gas mixture is syngas from a steam methane reforming reactor, the first component is carbon dioxide, the second component includes hydrogen, and the third component includes carbon monoxide and methane.

32. The process of claim 31, further recycling the product enriched in the third component to the steam reforming reactor.

33. The process of claim 32, further providing the feed gas mixture as syngas directly from the steam reforming reactor, without any intermediate step of processing in a water gas shift reactor.

FIG. 1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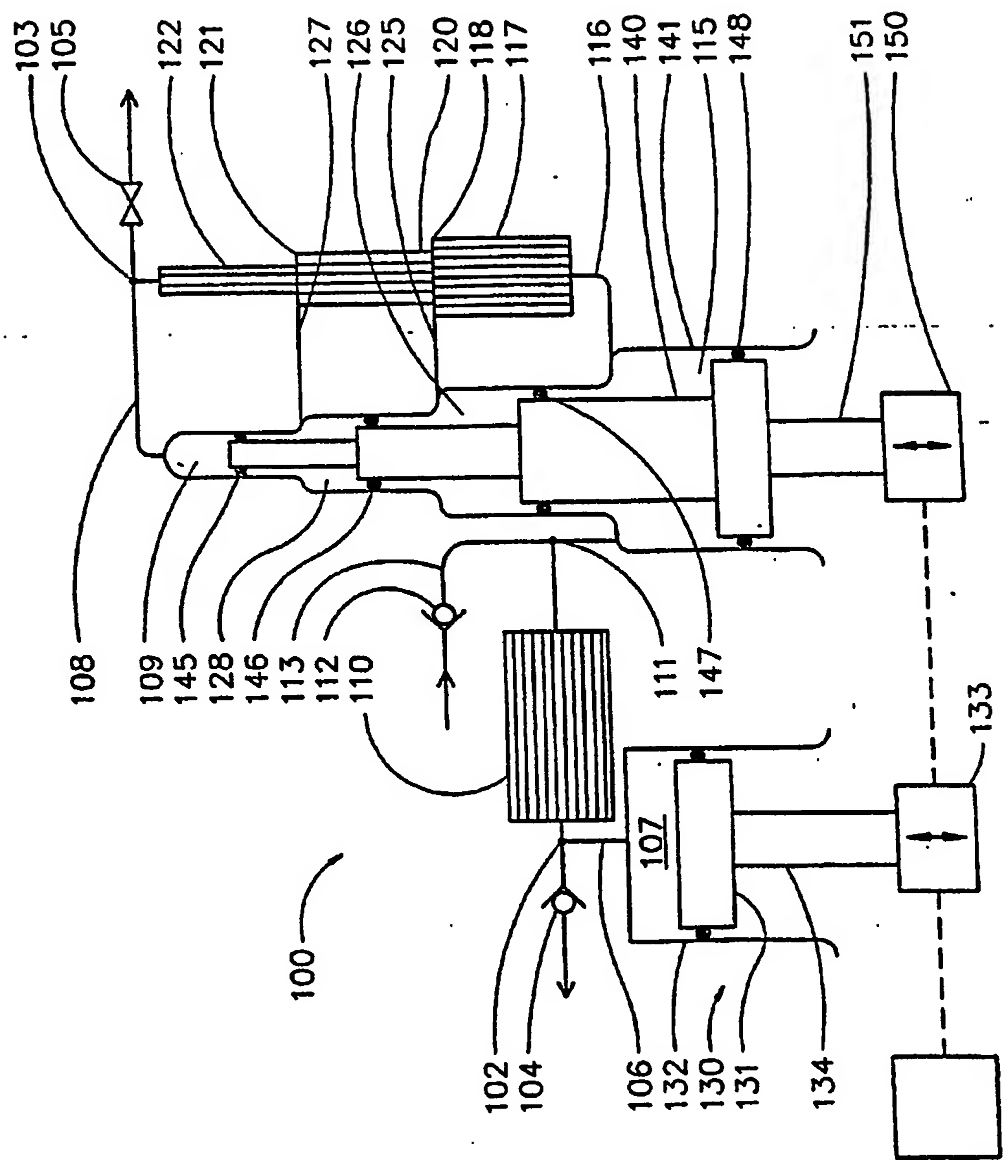
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FIG. 2

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FIG. 3

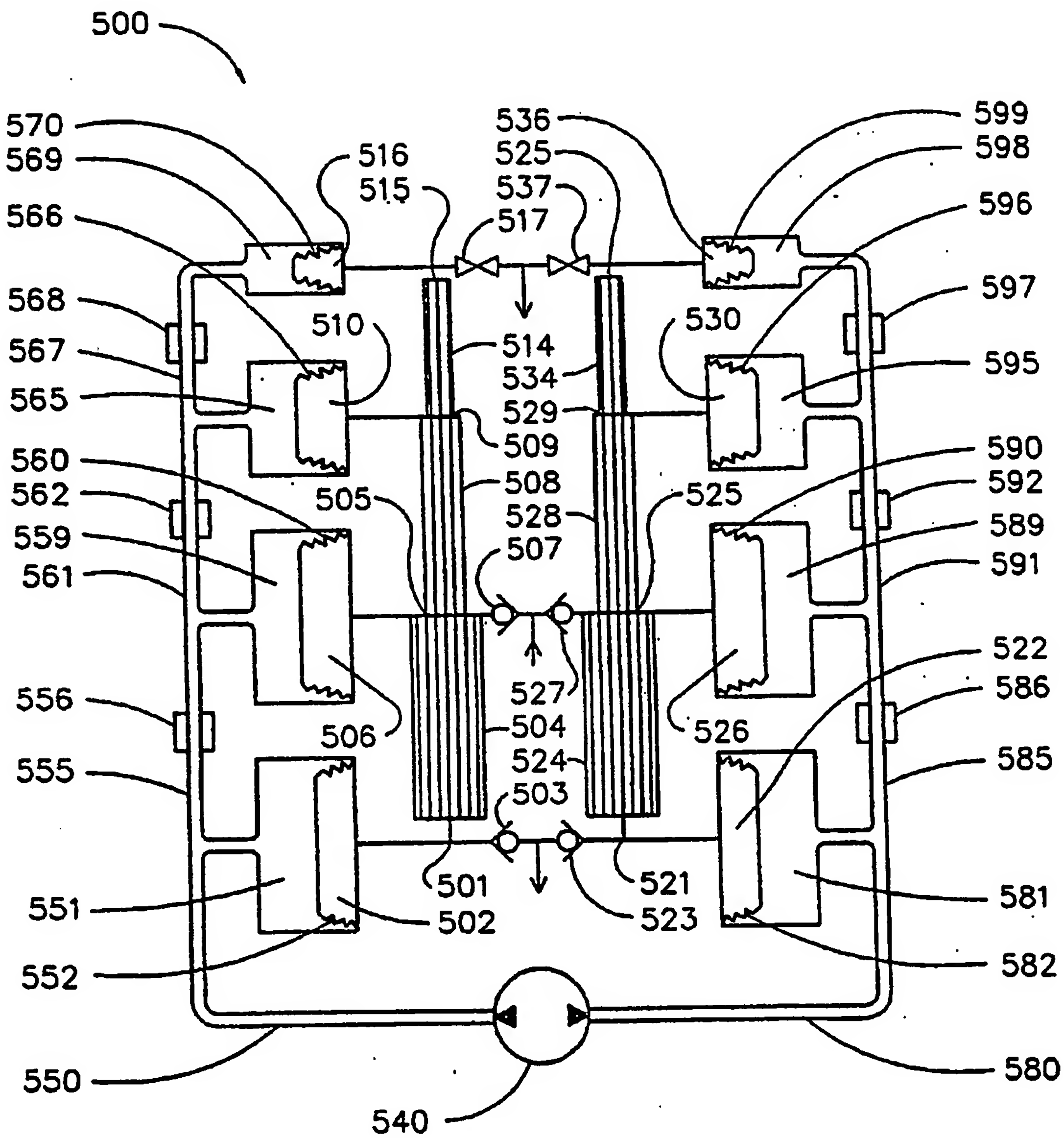
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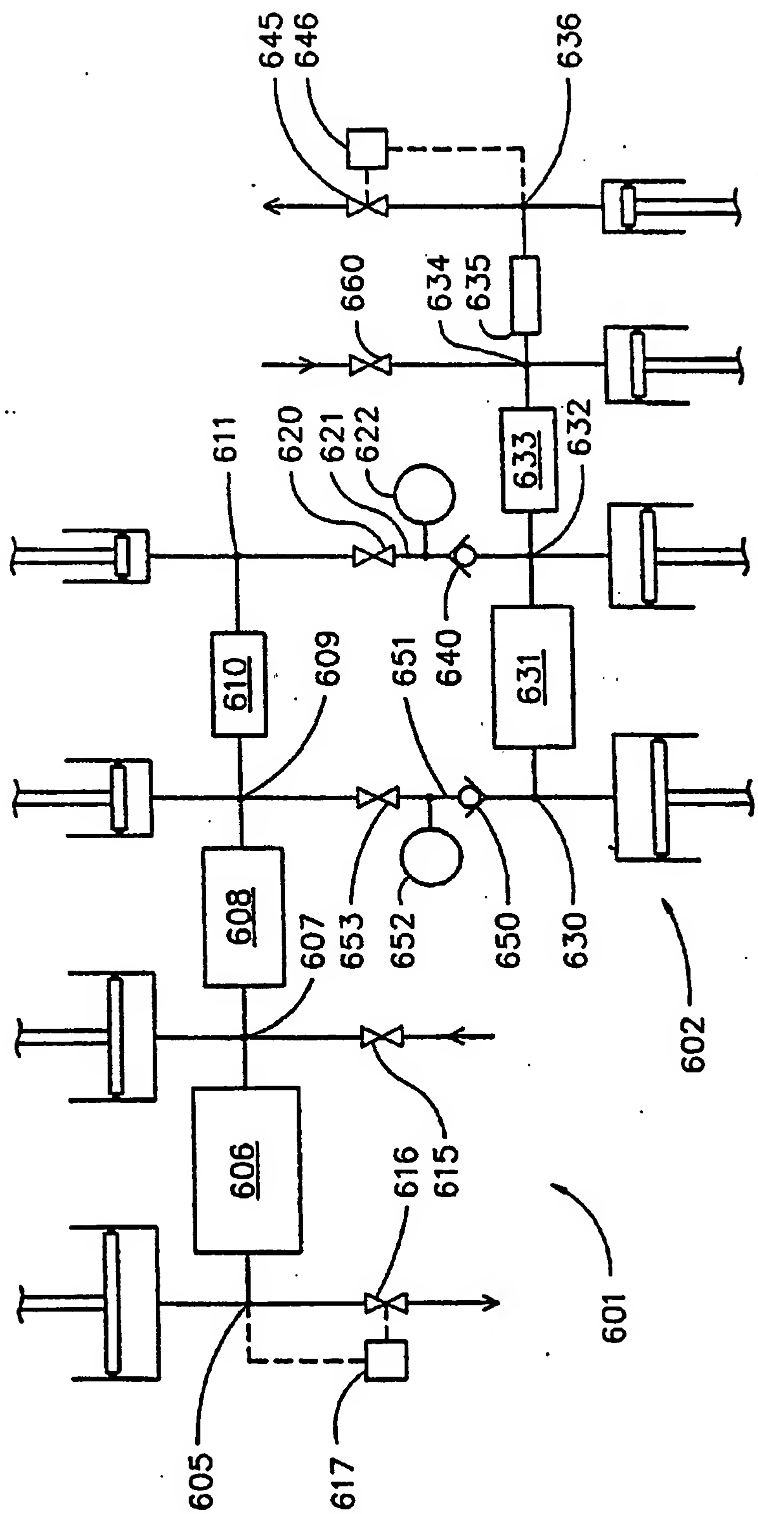
FIG. 4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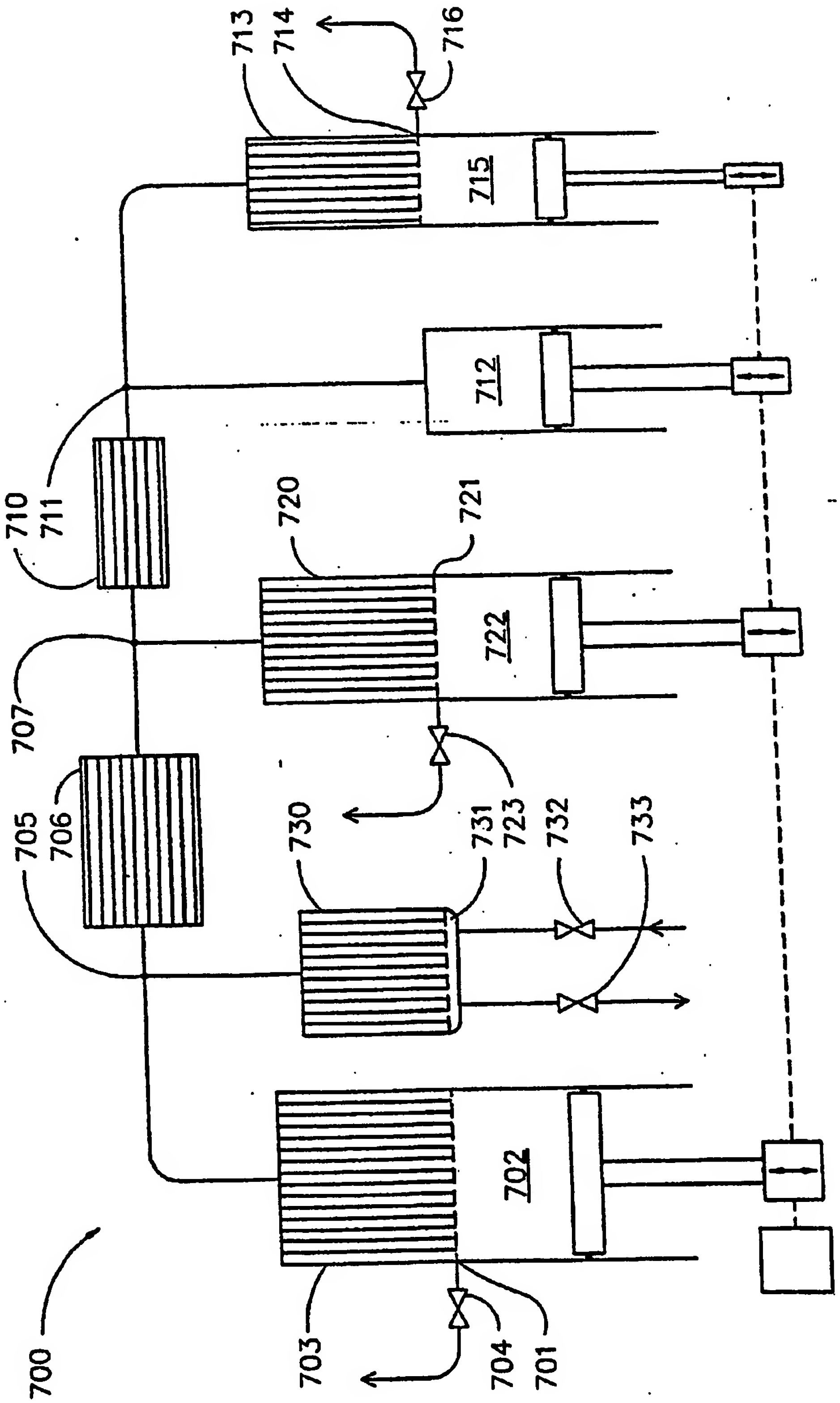
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FIG. 5